In-situ TEM Observation of Repeating Events of Nucleation in Epitaxial Growth of Nano CoSi₂ in Nanowires of Si

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ABSTRACT

The formation of CoSi and CoSi₂ in Si nanowires at 700 and 800 °C, respectively, by point contact reactions between nanodots of Co and nanowires of Si have been investigated in situ in a ultrahigh vacuum high-resolution transmission electron microscope. The CoSi₂ has undergone an axial epitaxial growth in the Si nanowire and a stepwise growth mode was found. We observed that the stepwise growth occurs repeatedly in the form of an atomic step sweeping across the CoSi₂/Si interface. It appears that the growth of a new step or a new silicide layer requires an independent event of nucleation. We are able to resolve the nucleation stage and the growth stage of each layer of the epitaxial growth in video images. In the nucleation stage, the incubation period is measured, which is much longer than the period needed to grow the layer across the silicide/Si interface. So the epitaxial growth consists of a repeating nucleation and a rapid stepwise growth across the epitaxial interface. This is a general behavior of epitaxial growth in nanowires. The axial heterostructure of CoSi₂/Si/CoSi₂ with atomically sharp epitaxial interfaces has been obtained. A discussion of the kinetics of supply limited and source-limited reaction in nanowire case by point contact reaction is given. The heterostructures are promising as high performance transistors based on intrinsic Si nanowires.

Nanostructures in Si nanowires have been studied for basic components in electronic and optoelectronics devices, especially biosensors.1–5 Well-defined nanoscale building blocks such as ohmic contacts and gates on Si nanowires must be developed in order to be assembled into functional electronic structures.6,7 It requires a systematic study of chemical reactions in the nanoscale to form these circuit components.8 Not surprisingly, the formation of silicane nanowire has been investigated recently and widely.9–19 When a Si nanowire touches a metal nanowire, a point contact is formed and the chemical reaction between them starts from the point of contact. We report here the point contact reactions between Si nanowires and Co nanodots investigated by in situ high-resolution transmission electron microscopy (HRTEM), which is a powerful means for the study of nanoscale kinetics.15–29 We have grown heterostructure of CoSi₂/Si/CoSi₂ with atomically sharp epitaxial interfaces. The metallic CoSi₂ may serve as the source-drain contacts to the Si in the heterostructure; it is the first step to produce a nanoscale field-effect transistor.30,31

We have selected Co and Si for our study since Co silicides possess very interesting and important properties. Single crystalline CoSi has ferromagnetic properties which were the focus of intensive research.32,33 The disilicide CoSi₂ is one of the three silicides which have the lowest resistivity for applications in shallow junction devices.12,34 The growth kinetics of Co silicide in nanoscale may be different from that in thin film and bulk samples.35 In this work, we observed a supply limited reaction of dynamic epitaxial growth in point contact reaction. More importantly, we have observed and recorded the nucleation stage in the epitaxial reaction to form CoSi₂. We shall be able to isolate the nucleation event and study the kinetic of nucleation in the future.

Si nanowires were prepared on a Si wafer by the vapor—liquid—solid method using nano-Au dots as catalyst for the growth of single crystal Si nanowires with [111]
We did not find a good epitaxial relation between CoSi and pattern, the silicide formed within Si nanowires was CoSi. From the selected area diffraction pattern, the silicide formed within Si nanowires was CoSi. We did not find a good epitaxial relation between CoSi and Si. As a result, the interface is rough. Comparing with NiSi formation within Si nanowire, NiSi was found to grow epitaxially on (111) Si with the following epitaxial relation; Si[1−10]//NiSi[1−12] and Si[111]//NiSi[31−1]. Therefore, the interface between NiSi and Si is atomically sharp. In addition, no misfit dislocations were found across the NiSi/Si interface.

Figure 1a,b shows that a Co particle (indicated by a blue arrow) disappeared within 0.07 s and the CoSi grew promptly within the same time period. If we assume the Co particle is spherical, the volume of the Co particle is about 1580 nm³. When such a volume of Co reacts with Si to form CoSi, the volume of the formed CoSi can be calculated to be 3500 nm³. Knowing the densities of Co and CoSi, which are 8.9 × 10⁻¹⁸ and 6.65 × 10⁻¹⁸ g/nm³, respectively, it was calculated that 2.40 × 10⁻¹⁶ mole of Co and 2.67 × 10⁻¹⁶ mole of CoSi participated in the reaction. Since the mole values are about the same, we conclude that the rapid disappearance of the Co particle led to the CoSi formation. From the finding that the instant reaction rate was much higher than the average growth rate in Movie 1 in Supporting Information, we conclude that the dissolution of a large number of Co atoms into the Si occurs in a short time, so the reaction rate is much faster. The consideration is based on the assumption that the Co particle has had a large contact area to the Si nanowire as the oxide layer might be thinner and the bonding might be weaker at the contact position. Although this is a special case, it provides us, however, the important information that the source of the CoSi is the Co particles on the surface of the Si nanowire. Nevertheless, for most of the Co particles, the point contact with a very small contact area will limit the reaction, so the overall growth of CoSi is much slower, as shown in Figure 1c.

Point contact samples were prepared by dripping droplets of solutions containing Si and Co nanowires on a Cu grid covered with a 50 nm thick amorphous SiO₂ film, which is transparent to the electron beam and does not interfere significantly with the images of Si and Co nanowires in HRTEM. The samples were dried at room temperature. In situ annealing for point contact reactions and high-resolution lattice imaging were performed and taken in a JEOL 2000V ultrahigh vacuum TEM. The vacuum in the sample stage was about 3 × 10⁻¹⁰ Torr.

Upon heating, the Co nanowires were prone to disintegrate and form Co nanodots on the oxidized surfaces of Si nanowires having about 2 nm thick surface oxide layer and also on the SiO₂ coating of the Cu grids. Figure 1a,b is the TEM image sequences of point contacts of a Si nanowire and several Co nanodots annealed at 700 °C. The typical diameters of the Si nanowire and the Co particles in Figure 1 are about 20 and 8 nm, respectively. Most likely the Co particles were formed by evaporation from the Co nanowires and condensation on the SiO₂ coating of the Cu grids. Many small Co particles were observed beside the Si nanowires and some of them were on the SiO₂ window, as shown in Figure 1. In the Si nanowire, the dark region on the left-hand side is Co silicide. From the selected area diffraction pattern, the silicide formed within Si nanowires was CoSi. We did not find a good epitaxial relation between CoSi and Si growth direction. The Si nanowires were detached from the wafer in ethanol solution by ultrasonic vibration. Poly-crystalline Co nanowires were synthesized by electroplating Co into a porous anodic aluminum oxide (AAO) template structure and then the AAO template was etched away to obtain Co nanowires. Finally the nanowires of Co were stored in isopropanol solution. Both the Co nanowires and Si nanowires have diameters ranged from 20 to 70 nm and lengths of a few microns.

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due to the interaction at the triple point between the Co particle and the SiO\textsubscript{2} surface.

How to control the amount and arrangement of Co nanodots is a challenging question. At the moment, we are preparing a regular array of Co nanodots by patterning for a future study of their reaction with Si nanowires.

Figure 3a is a HRTEM image of a sharp epitaxial CoSi\textsubscript{2}/Si interface. The darker and brighter regions show the atomic layers in CoSi\textsubscript{2} and Si, respectively. The crystallographic orientation relationships between the Si and CoSi\textsubscript{2} are Si[110]/CoSi\textsubscript{2}[110] and Si(111)/CoSi\textsubscript{2}(111) (see the selected area electron diffraction patterns of Si and CoSi\textsubscript{2} in the inset), which show the direction [110] on (111) plane of CoSi\textsubscript{2} is parallel to the direction of [110] on (111) plane of Si. The Si and CoSi\textsubscript{2} are of diamond and CaF\textsubscript{2} structures with lattice parameters of 0.5432 and 0.5365 nm, respectively. Since the structures of CoSi\textsubscript{2} and Si are cubic and with small lattice mismatch (1.2%), Si (111) can have a good epitaxial relation with CoSi\textsubscript{2} (111); therefore, CoSi\textsubscript{2} has a preferential epitaxial orientation with Si to form a sharp interface. Since the structures differ for CoSi and CoSi\textsubscript{2}, which are respectively BCC and CaF\textsubscript{2}, the degree for epitaxial growth of CoSi and CoSi\textsubscript{2} on Si are different so that there is much difference for the sharpness of their interfaces. The phase of Co silicide can be determined by selected area diffraction and by the morphology of the interface. CoSi\textsubscript{2} is a higher temperature phase and CoSi is a lower temperature phase, which was reported for thin film experiments.\textsuperscript{39} If we apply the thin film results to our nanowire case, it explains our finding of different temperatures for the formation of nano CoSi and CoSi\textsubscript{2}. Figure 3b is a TEM image of CoSi\textsubscript{2}/Si/CoSi\textsubscript{2} heterostructure with the middle Si region of 90 nm in thickness.

The growth rates of CoSi\textsubscript{2} within the Si nanowire at 800 °C can be measured from in situ HRTEM video, which shows that the CoSi\textsubscript{2} grows atomic layer by atomic layer. During the growth of an atomic layer, the growth mode behaves as the moving of steps or kinks across the interface, as shown in Figure 4a–d. From the video (Movie 2 in Supporting Information), however, we found that there is a long period of stagnation between the stepwise growths of two successive atomic layers. When we plot the stagnation period as well as the growth period, we obtained the staircase curve as shown in Figure 5a. It shows that the growth rate of each of the CoSi\textsubscript{2} atomic layer is the same, which is \(\sim 0.17\) s per layer, and it is just the width of the vertical line in the Figure 5a. In between the vertical lines (the horizontal part of the steps in Figure 5a) is the stagnation period, which we define as the incubation time of nucleation of a new layer. The average value of the incubation time is about 5 s. In other words, while the motion of a step or a kink across the cross-section of the nanowire is the same, the intervals between the growths of atomic layers are not the same, indicating that the incubation time of the nucleation of a step or a kink on the cross-section can be different, as shown in Figure 5a that the length of the horizontal part are different. For comparison, Figure 5b shows three recorded stair-type of axial epitaxial growth of CoSi\textsubscript{2} in Si nanowire.
The average growth rate of CoSi$_2$ along the axial direction is 0.0365 nm/sec. From Figure 4, the radial growth rate, step velocity, could be calculated to be about 135 nm/sec. It is remarkable that the radial growth rate is about 3700 times faster than that of the axial growth rate. This is because the measured average axial growth rate has taken into account the incubation time of nucleation of every step. The fast radial growth of CoSi$_2$ seems to follow its nucleation from the center of the nanowire. Due to surface oxide of the Si nanowire, it is likely that the energy of the interface of CoSi$_2$/SiO$_2$ is higher than that of Si/SiO$_2$, so the frequency of heterogeneous nucleation at the edge is low, and the nucleation of a step at the center of the wire becomes possible. Another reason is that there may exist a heterogeneous defect at the center of the interface which favors a step nucleation.

Without including the incubation time of nucleation, on the basis of the measured radial growth rate of 135 nm/sec, the axial growth rate of each CoSi$_2$ atomic layer is about 1.82 nm/sec. This result shall be obtained by using the following equation as well

$$V = Nevh$$

where $V$ is axial growth rate, $v$ is radial growth rate, $N$ is number of steps per unit length, and $h$ is the height of the step. However, this equation fails in epitaxial growth in nanowires when there is a long period of stagnation between each CoSi$_2$ layer growth.

A comparison of growth kinetics of Co silicides and Ni silicides in thin film reactions is shown in Table 1. The activation energy of Co silicide formation in thin film reactions is much higher than that of the Ni silicide. If we apply the experience in thin film case to our nanowire case, the formation of Co nano silicide needs higher activation energy, which is perhaps the reason of the slower growth rate of CoSi$_2$ than that of NiSi. We have reported the linear growth rates of axial epitaxial NiSi in nanowires of Si in the temperature range of 500–700 °C. On the basis of the observation shown in Figure 5, we expect that the linear growth of NiSi should show the stair-type behavior, so the nucleation event and the growth event can be studied separately.

In samples annealed at 700 and 800 °C, the Co particles appear beside the Si nanowires and on the SiO$_2$ window. These Co particles seemed to be stable in annealing. Here, we eliminate the possibility of surface diffusion in forming Co particles and Co silicides since we found no change in the distribution of the size of Co particles after 50 min at 800 °C. In other words, there is no ripening among the Co particles, as shown in Figure 6a,b.

In bulk and thin-film interfacial reactions, there are diffusion-limited and interfacial-reaction-limited reac-

**Table 1.** Comparison of Co–Si and Ni–Si Systems$^{42}$

<table>
<thead>
<tr>
<th>System</th>
<th>Structure</th>
<th>Activation energy (eV/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co–Si</td>
<td>CoSi BCC</td>
<td>~2.03</td>
</tr>
<tr>
<td></td>
<td>CoSi$_2$ CaF$_2$</td>
<td>~2.81</td>
</tr>
<tr>
<td>Ni–Si</td>
<td>NiSi orthorhombic</td>
<td>~1.25</td>
</tr>
<tr>
<td></td>
<td>NiSi$_2$ CaF$_2$</td>
<td>~1.5</td>
</tr>
</tbody>
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![Figure 4](image-url) In situ HRTEM image sequences of growing CoSi$_2$/Si epitaxial interfaces within Si nanowires. (a–d) the growth of 1 atomic layer has occurred, and the step is indicated by the arrow. The left-up and right-down regions are close to center and edge of nanowire, respectively.

![Figure 5](image-url) Plot of CoSi$_2$ atomic layers as a function of time to show the nucleation time and growth time of each step. (a) One stair-type growth curve of CoSi$_2$. (b) Three sets of stair-type growth curve of CoSi$_2$.

![Figure 6](image-url) TEM images showing that no ripening occurred at 800 °C after 50 min annealing.
In point contact reactions, we shall consider supply limited reaction since it can be the slowest kinetic process in the reaction. Let \( J \) be the dissolution flux from a nanowire or a nanoparticle of Co into a Si nanowire, and the unit of \( J \) is the number of atoms/cm²·sec. Let \( \delta A \) be the area of a point contact. Thus in a period of \( t \), the number of Co atoms dissolved into the Si nanowire is \( J(\delta A)t \). The growth of CoSi or CoSi₂ will consume the dissolved Co atoms. If we assume the cross-sectional silicide/Si interface area is \( A \), and \( v \) is the linear growth rate, we have by mass conservation that

\[
J(\delta A)t = CVtA
\]

where \( C \) is the concentration of Co in the silicide, and we have

\[
J(\delta A)/A = CV \tag{2}
\]

We note that eq 2 is similar to the conventional flux equation of \( J = C\mu/\nu \) where \( \mu/\nu \) is drift velocity, except that the rate in eq 2 is limited by \( \delta A \) when it is a point in point contact reaction. A constant reaction rate is expected and the rate constant will be limited by \( \delta A \). In our experiments, the contact region of Co nanodots and Si nanowire is a small area and it only allows a very limited amount of flux of Co atoms to diffuse into the Si nanowire per unit area per unit time, so the silicide phase formation depends on the supply of Co.

In our experiment, the HRTEM video shows that the overall growth rate of CoSi₂ layers is linear, yet we can decompose the linear curve into many stair-steps where the step height equals to an atomic layer thickness. There was a stagnation period for a new layer to form, and the time interval between every step was varying. It takes an incubation time to create a new step. When a step was created, it propagated very quickly across the Si/CoSi₂ interface. So the overall reaction rate was limited by the nucleation stage, and it is linear with time. In nucleation, it might need to wait for enough Co atoms to diffuse into Si nanowires to reach supersaturation in order to nucleate a CoSi₂ step. So the supply limited dissolution of Co into the Si at the point contact may become rate limiting.

The atomically sharp NiSi/Si interface in Si nanowires has previously been reported.⁷,⁹ The movement of the NiSi/Si interface producing 2 nm Si region was observed in situ.⁹ In the present study, not only the stepwise axial growth but also lateral growth of atomic step at the CoSi₂/Si interface was observed. In addition, the nucleation and growth stages of each layer of the epitaxial growth were well resolved in video images. As the resolution of nucleation and growth is one of the most challenging problems in phase transition of condensed matters, the study has provided unique and significant insight on the growth mechanism of an important system in nanotechnology.

NiSi/Si/NiSi nanowire heterostructures have been reported by several groups.⁷,⁹,¹¹ Silicon nanowire transistors have been fabricated for these heterostructures.⁷,¹¹ However, in these reports, chemically doped silicon nanowires are used in order to ensure a reasonable source-drain contact and decent transistor characteristics. On the other hand, a very recent work for PtSi/Si/PtSi transistors based on intrinsic Si nanowires has achieved high performance normally off transistors.⁴ In addition, sub-100 nm channel length Ge/Si nanowire transistors contacted with nanoscale NiSi₆Ge₇ layer showing potential for 2 THz switching speed were reported. It also showed small geometry contact as in the axial heterostructure is advantageous for device performance.⁴⁶ As CoSi₂ is one of the few available low-resistivity silicides for metallization in sub-100 nm devices, its implementation is compatible with the present devices fabrication technology.¹² As a result, high performance CoSi₂/Si/CoSi₂ transistors based on intrinsic Si nanowires shall be highly desirable for future nanoelectronics applications and are currently under investigation.

In summary, Si nanowires transformed into CoSi and CoSi₂ by point contact reaction between Co nanodots and Si nanowires at annealing temperatures of 700 and 800 °C, respectively. The CoSi₂ has axial epitaxial relation with Si, and HRTEM images show that the interface between CoSi₂ and Si is very sharp. A layer by layer stepwise growth was found in which we can resolve the nucleation stage and the growth stage. In addition, lateral growth in the form of an atomic step sweeping across the CoSi₂/Si interface was observed. The repeating nucleation stages of CoSi₂ in the epitaxial reaction have been observed and the incubation time recorded. In point contact reactions, we propose that it can be limited by the supply of Co atoms or the dissolution of Co into the Si via the point contact area. Single crystal CoSi₂/Si/CoSi₂ heterostructure with sharp interfaces can be made by this method. The heterostructures are promising as high performance transistors based on intrinsic Si nanowires.

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Supporting Information Available: TEM videos of the reaction of a Co nano dot and Si nanowire and high resolution TEM video of CoSi₂ stepwise growth. Supplementary Movie 1. An in situ TEM movie, taken at 700 °C in vacuum better than 10⁻⁹ Torr, shows the dissolution of a large number of Co atoms into the Si occurs in a short time with the reaction rate being much faster than the actual speed. The time of the image captured is given at the upper-left corner. The first two numbers are in unit of minutes and the following two numbers are in unit of seconds. Scale bar is included in every image (Quick Time; 2.49 MB). Supplementary Movie 2. A high resolution in situ TEM movie, taken at 800 °C and in vacuum better than 10⁻⁹ Torr, shows the CoSi₂/Si epitaxial interface grows atomic layer by atomic layer within a Si nanowire, and there is a long period of stagnation between the stepwise growths of two successive layers. The image sequence from Figures 4a–d is extracted from this movie. The time of the image captured is given at the upper-left corner. The first two numbers are in unit of minutes and the following two numbers are in unit of seconds. Scale bar is included in every image (Quick